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Counting ^{81}Kr Atoms for Analysis of Groundwater

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A new analytical technique with sufficient sensitivity to determine ^{81}Kr concentrations in groundwater is described. The method utilizes single-atom counting by laser resonance ionization spectroscopy (RIS) in combination with a small mass spectrometer to achieve the required selectivity and sensitivity. A first demonstration of the technique for groundwater analyses is presented in which about 1000 atoms of ^{81}Kr were counted after the processing of gas extracted from only a few liters of water. The potential of the new method for groundwater dating in the range 50,000 to 1,000,000 years is discussed.

1. INTRODUCTION

A new long-lived krypton activity was first found by *Reynolds* [1950] after intense neutron irradiation of a bromine target. After analysis by mass spectrometry and decay counting, he concluded that the radioactive noble gas isotope ^{81}Kr had been produced by n capture from ^{80}Kr and that its half-life was 210,000 ($\pm$50,000) years. A remeasurement of the half-life by *Eastwood et al.* [1964] yielded 213,000 ($+$16,000/$-$ 26,000) years, in excellent agreement with the first determination. Cosmic-ray-produced ^{81}Kr was first detected by *Marti* [1967] in a meteorite with high concentrations of strontium, yttrium, and zirconium, from which ^{81}Kr was produced by spallation. Krypton-81 radiation ages of meteorites [*Eugster et al.*, 1967] and lunar material [*Eberhardt et al.*, 1970] were subsequently determined with highly sensitive mass spectrometers.

In the earth's atmosphere, ^{81}Kr is produced by cosmic rays in p-, n-, or γ-induced spallation reactions from the stable isotopes ^{82}Kr, ^{83}Kr, ^{84}Kr, and ^{86}Kr and by neutron capture by ^{80}Kr. The atmospheric specific activity is extremely low. It was first measured by *Loosli and Oeschger* [1967] to be 0.1 ($\pm$10%) dpm/L krypton. The measured value is in general agreement with an estimated global production rate given by *Oeschger et al.* [1970] for a constant cosmic ray flux. A recent remeasurement of the ^{81}Kr atmospheric activity by *Kuzminov and Pomansky* [1983] yielded a value of 0.076 ($\pm$0.004) dpm/L krypton. They discussed the nuclear reactions that produce ^{81}Kr in the atmosphere in detail and calculated a theoretical value for the production rate of 0.060 ($\pm$0.013) dpm/L krypton which also led them to conclude that the present atmospheric ^{81}Kr activity is in agreement with the assumption of constant average ^{81}Kr production over the last 100,000 years. Giving equal weight to the two independent ^{81}Kr activity measurements [*Loosli and Oeschger*, 1967; *Kuzminov and Pomansky*, 1983], we take a value of 0.088 dpm/L krypton for the following discussion and assume a corresponding Kr/^{81}Kr ratio in modern air of 1.9×10^{12}, where Kr represents all isotopes of krypton.

It has long been recognized that ^{81}Kr could be used for dating groundwater or polar ice core samples in the range 50,000 to 1,000,000 years. A ^{81}Kr-based technique would considerably extend the range that is accessible to ^{14}C dating and is expected to have definite advantages over other dating methods because of (1) the inert chemical character of krypton, (2) the fact that the atmosphere is the main reservoir with a concentration that has probably been constant for a long time, and (3) the expectation that underground production should be small (Workshop on Dating Old Groundwater, U.S. Department of Energy, Tucson, Arizona, 1978; *Davis and Bentley* [1981]).

With a solubility of krypton in groundwater of 9.2×10^{-5} cc of krypton per liter of water (10°C) and a Kr/^{81}Kr ratio of 1.9×10^{12}, we expect to find only 1300 atoms of ^{81}Kr in 1 liter of modern water. Because of this very low concentration, it has been impossible to use this isotope in geophysical studies. Even the best low-level decay counting techniques would require hundreds of tons of water. Furthermore, contamination with as little as 0.1% of modern air would add enough ^{85}Kr activity to completely mask the ^{81}Kr signal [*Lehmann and Loosli*, 1984].

Obviously, it would be very desirable to have a technique for counting ^{81}Kr atoms directly rather than having to wait for their decay. The recently developed accelerator-based atom-counting systems have successfully been used for several cosmic-ray-produced radioisotopes, such as ^{14}C, ^{10}Be, and ^{36}Cl in geophysical studies [*Suter et al.*, 1985; *Beer et al.*, 1984; *Finkel et al.*, 1980]. They cannot be used, however, for ^{81}Kr analyses because krypton does not easily form negative ions for use in a tandem accelerator. Cyclotron machines operating with Kr^+ ions could, in principle, be used for noble gas work, but the current estimates for sample size again are in the range of several hundred thousand liters of water (Workshop on Dating Old Groundwater, Tucson, Arizona, 1978).

Our approach to count the number of ^{81}Kr atoms in a water sample of a few liters is based on resonance ionization

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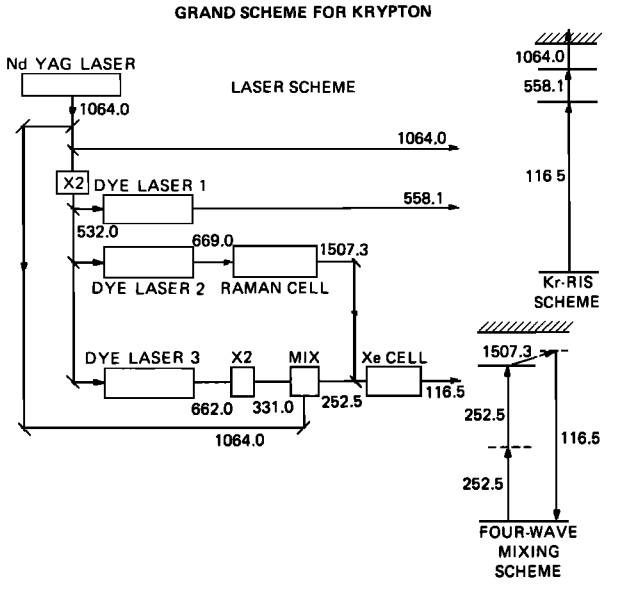

Fig. 1. Resonance ionization spectroscopy scheme and method of generating required wavelengths for krypton.

spectroscopy (RIS). Three steps are involved: (1) degassing of water and separation and purification of noble gases, (2) two cycles of isotope enrichment, and (3) ^{81}Kr atom counting based on RIS.

2. Sample Processing

We extract air from a groundwater sample by bubbling helium gas through the water and trapping the extracted air in a liquid-nitrogen-cooled charcoal trap. Noble gases are then separated and purified by using getter techniques and gas chromatography. From one liter of water, we expect more than 10^{15} atoms of krypton and only 1300 or less atoms of ^{81}Kr. Such a krypton gas sample cannot immediately be introduced to the ^{81}Kr counter because the ^{82}Kr/^{81}Kr ratio of 2.2×10^{11} in a natural modern krypton sample is too large to be resolved by the relatively simple mass filter in our detector system. Therefore the level of neighboring isotopes (^{82}Kr, ^{80}Kr) must first be reduced by isotope enrichment.

The number of spurious counts at mass m due to neighboring isotopes ($m \pm 1$) leaking through the mass discriminator represents a counting error. In order to count 1000 atoms of ^{81}Kr with an acceptable counting error of 10% and with a mass filter abundance sensitivity of 10^5, the number of ^{82}Kr atoms must be reduced to 10^7 [*Willis and Thonnard*, 1984].

To achieve this level of enrichment, we use the concept of an atom bank, where atoms of a selected isotope can be deposited and be withdrawn after unwanted species have been pumped out of the system. Ions of ^{81}Kr are implanted at 10 kV into a target and are subsequently recovered either by laser evaporation or laser annealing.

In the first enrichment cycle, ions were implanted into aluminized Kapton foil and recovered by evaporating the aluminum coating with a pulse of second harmonic light (532 nm) of a Nd:YAG laser. In the second enrichment cycle, ions were implanted into high-purity silicon and recovered by annealing the silicon surface by scanning with a focused beam of second harmonic Nd:YAG pulses.

Kapton is relatively easy to handle, but impurity problems prevent us from using it in the second cycle. The silicon annealing is a cleaner method, but details of the annealing mechanism are still being studied and the requirements for laser beam quality are higher. In each enrichment cycle the ^{82}Kr/^{81}Kr ratio is reduced by at least 3 orders of magnitude.

3. ^{81}Kr Detection by Resonance Ionization Mass Spectroscopy

Laser RIS combines the selectivity of optical spectroscopy with the sensitivity of ionization detectors. Using pulsed tunable lasers to ionize atoms of a selected element enables single atom detection in as many as 10^{19} background atoms or molecules. The RIS technique has been developed at the Oak Ridge National Laboratory, and several review articles on the general aspects as well as on particular applications of the method have been published [*Hurst et al.*, 1979, 1980, 1985]. RIS can, in principle, be used to detect any element of the periodic table except helium and neon, and this has actually been proven by experiment in the last few years for about half of them [*Travis et al.*, 1984]. However, systems for the detection of elements with high ionization potentials are significantly more complex than those for alkali metals, for example. Whereas an element like cesium can be excited and ionized with a single laser pulse of 455.5-nm light, it is necessary to produce tunable vacuum ultraviolet light to excite even the lowest state in krypton. Since no commercial systems are available at this time in this wavelength region, we had to develop our own light source.

We use a commercial Nd:YAG laser-based system to produce up to 700 nJ per pulse at 116.5 nm tc selectively excite krypton atoms from the ground state to the $4p^5 5s(1/2)_1$ state. The arrangement makes use of several nonlinear optical processes such as frequency doubling, frequency mixing, Raman shifting, and four-wave mixing (Figure 1). A second resonant step at 558.1 nm promotes krypton atoms to the $4p^5 6p(1/2)_0$ state, and ionization is completed by residual light of the Nd:YAG fundamental at 1064 nm. Details of the optical system are given by *Kramer et al.* [1983]. Since isotope effects in atomic spectra are small and we work with relatively broadband light (1.5 cm^{-1} at 116.5 nm), all isotopes of krypton are ionized simultaneously. In order to get isotopic selectivity, the RIS technique is combined with a conventional mass spectrometer. For xenon this had already been demonstrated by *Chen et al.* [1980].

In Figure 2 we show a schematic of the detector arrangement. The RIS laser beams are directed to a point in front of the entrance aperture of a commercial quadrupole mass filter (Extranuclear). Ions are extracted into the mass filter, and ions of the selected mass are accelerated to 10 kV as they leave the exit aperture. Secondary electrons emitted from a CuBe target are then counted with an electron multiplier.

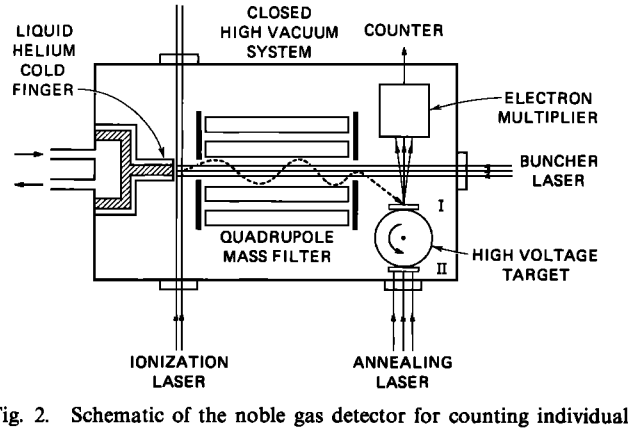

Fig. 2. Schematic of the noble gas detector for counting individual atoms.

With our best RIS scheme we can only ionize all krypton atoms in a volume of about 5×10^{-4}cm^3. The probability of ionization for one krypton atom in our closed system of $\sim$3000 cm^3 is, therefore, only 1.67×10^{-7} per pulse. In other words it would require 6×10^6 pulses for a one *e*-fold counting or about 280 hours at a repetition rate of 6 Hz. Obviously, such a system would not be very effective. Therefore we developed an "atom buncher," consisting of a very well defined liquid-helium-cooled cold spot just below the focal point of the RIS lasers. Krypton atoms are continuously trapped on this cold surface and can be released by a 1-μs pulse from a flashlamp-pumped dye laser fired along the axis of the quadrupole mass filter about 5 to 10 μs before the RIS lasers fire. In this way we are able to release keypton atoms in "bunches" into the ionization laser beams, and we can increase the probability of ionization for one atom per pulse by a factor of about 500. We can then count ^{81}Kr atoms (one *e*-fold) in less than 1 hour. Technical details of the buncher design have been reported earlier [*Hurst et al.*, 1984].

The outgassing rate of krypton in the vacuum enclosure was about 1000 atoms of ^{84}Kr per minute. A titanium-zirconium getter pump (SAES) maintained a pressure in the 10^{-9} mbar range in the closed system. The abundance sensitivity of the quadrupole filter, when operated with the pulsed laser ionization and the atom buncher, is quite high and can reach values of at least 10^5. Therefore interferences in mass channel 81 due to outgassing of ^{82}Kr was not a problem in our measurements. We have demonstrated earlier that 1000 atoms of ^{81}Kr in a highly diluted standard gas supplied by the National Bureau of Standards (NBS) can actually be counted one by one [*Kramer et al.*, 1984; *Chen et al.*, 1984]. Additional technical details of the ^{81}Kr detector are discussed extensively in a review article by *Hurst et al.* [1985].

4. A First Demonstration of ^{81}Kr Analysis on a Groundwater Sample

We used a small fraction of gas that was extracted from about 10,000 liters of water for ^{39}Ar dating from a sandstone aquifer near Zurich, Switzerland (AQUI). The first cycle of isotope enrichment was performed in a quadrupole system by using its conventional electron-impact ion source. Since the throughput and the abundance sensitivity of such a system deteriorate at higher pressures, we only filled the 3-L volume to 6×10^{-6} Torr, implanted ^{81}Kr for 1 hour, and pumped the rest of the gas out of the system. This step was repeated 10 times to collect a total of approximately 1500 atoms of ^{81}Kr, a number that was calculated on the basis of pressure and ion current measurements and by assuming a modern ^{81}Kr level. The total amount of sample we processed was 2×10^{-4}cc of krypton, of which 55% was actually used, and the rest was pumped out of the system.

When working at this relatively high pressure, the ion source gets contaminated with krypton [*Willis et al.*, 1984], and the system cannot immediately be used for a second cycle of enrichment to reduce ^{82}Kr by another three orders of magnitude. Therefore we had to disassemble the ion source and electropolish all parts. After this procedure and appropriate baking of the system, the aluminum coating on the Kapton foil was evaporated by a laser pulse to release the remaining krypton atoms. The second enrichment step took 1 hour. This time, ^{81}Kr was implanted into a silicon target which was next introduced to the ^{81}Kr detector (Figure 2), where krypton atoms were released by laser annealing.

Figure 3 shows the mass spectrum after annealing, taken on

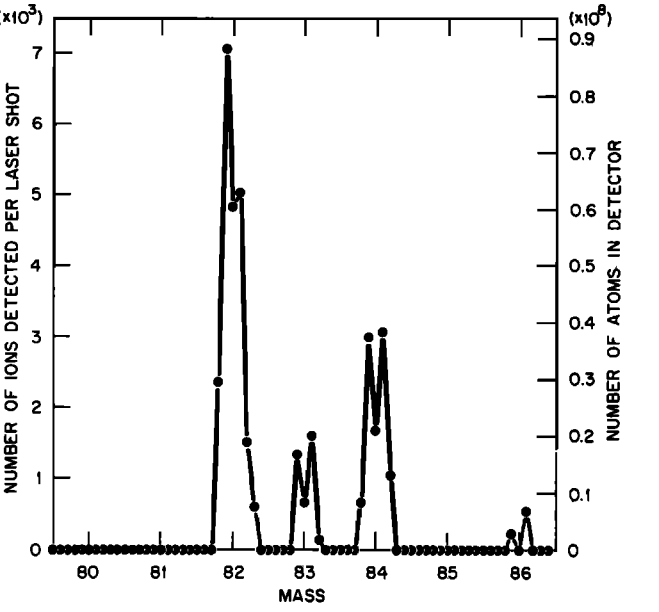

Fig. 3. Mass spectrum of krypton atoms released from a silicon target by laser annealing.

a sensitivity scale that does not reveal the small number of atoms at mass 81. As expected, mass 82 is the dominant isotope, and the number of ^{82}Kr atoms agrees with an estimated enrichment factor of $\sim (2000)^2$ in two cycles. Calibration of the analog signal is based on a multiplier gain calibration using ^{81}Kr standard gas. Figure 4 displays the mass 81 region with greater sensitivity. We had originally planned to run a third cycle of enrichment in the ^{81}Kr detector, but due to the very good abundance sensitivity of the quadrupole system when operated with the laser/buncher ion source, we were able to detect ^{81}Kr atoms without another cycle of enrichment. It is very easy to check if the signal at mass 81 is indeed produced by krypton atoms, since with a slight detuning of

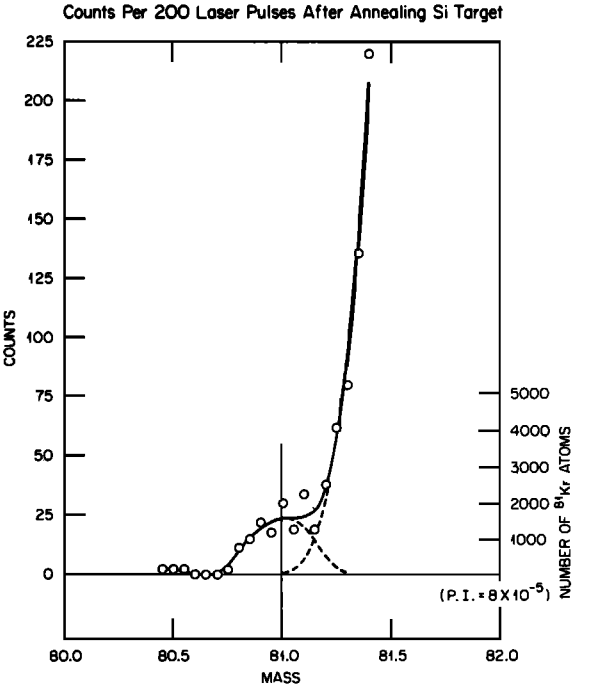

Fig. 4. Counts per 200 laser pulses for same sample as in Figure 3, amplified in the 81 mass region.

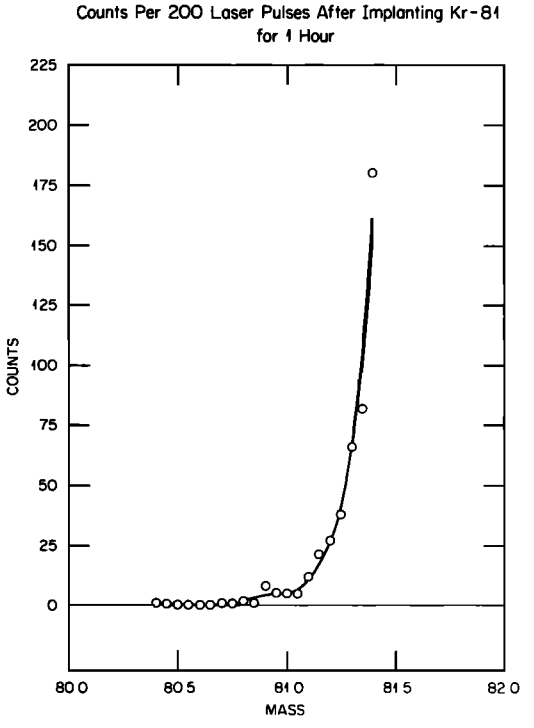

Fig. 5. Counts per 200 laser pulses after implanting ^{81}Kr for 1 hour.

3–4 Å of the yellow light (558.1 nm; second resonant step in the RIS scheme) the signal decreases to the background level, which was ~ 5 counts per 200 laser pulses in this situation. Our calibration of the number of atoms of ^{81}Kr is based on an ionization probability per pulse of 8×10^{-5}, which was determined by using the NBS ^{81}Kr standard gas; the signal at mass 81.0 represents 1200 (±300) atoms of ^{81}Kr.

We then implanted mass 81 for 1 hour into a silicon target. As can be seen in Figure 5, ^{81}Kr atoms indeed were thereby removed from the system. The ^{82}Kr level remained unchanged. The observed decrease of the ^{81}Kr signal after 1 hour of implantation is in agreement with our value for the ionization probability from which we calculate a one e-fold counting time of 35 min at a pulse repetition rate of 6 Hz.

5. Summary and Outlook

We have demonstrated for the first time that ^{81}Kr atoms originating from a groundwater sample of only a few liters can be detected. The complete chain of sample processing, including sampling and degassing of water, separation and purification of noble gases, two cycles of isotope enrichment, and the final detection of ^{81}Kr atoms, has been successfully completed. The procedure does not allow for any direct monitoring of ^{81}Kr until the final counting step. The fact that we were able to detect 1200 (±300) atoms of ^{81}Kr from an initial calculated level of 1500 atoms proves that losses in the two isotope enrichment cycles, where ions are implanted into and recovered from different targets, can be kept reasonably small. Since these losses are not yet quantified and since the overall accuracy was not very high in this first demonstration, it is too early to assign and "age" to our ^{81}Kr determination. We might, at best, estimate a rough upper limit for the age of this sample or get a preliminary indication that ^{81}Kr underground production in this sandstone aquifer is small.

In order to make the step from a first demonstration of the technique to a ^{81}Kr dating method, we now concentrate our efforts on the following aspects: (1) Since the enrichment procedure we had to use for this first demonstration is certainly inadequate for more routine measurements, we have built a new facility for the first enrichment cycle by using a commercial isotope enricher (COLUTRON) with a plasma ion source and a velocity filter to reduce all unwanted krypton isotopes by a factor of at least 10,000. The second cycle of enrichment is now performed in a separate quadrupole system, which is never used at high krypton pressures. The overall enrichment factor will be at least 10 times larger than in this first demonstration and will enable us to completely separate the ^{81}Kr signal from ^{82}Kr interference in the counting step. (2) Relative calibration will be achieved by using ^{78}Kr as an internal standard. The initial modern ^{78}Kr/^{81}Kr ratio of 6.0×10^{9} will be reduced by a factor of 200 in each enrichment step by simply switching for short time intervals from channel 81 to channel 78. A total of about 10^{8} atoms of ^{78}Kr, together with 1000 atoms of ^{81}Kr, will be introduced to the counting system. A ^{78}Kr/^{81}Kr ratio measurement will then be the basis for dating applications where only isotope ratios are needed.

With an improved calibration and with the capability of processing samples in a more routine procedure, we will investigate the potential of this new isotope for dating polar ice core and groundwater samples in the range 50,000 to 1,000,000 years. Deep polar ice cores from the Greenland and Antarctic ice shields contain an invaluable record of past climatic conditions, probably extending several hundred thousand years into the past. Establishing a chronology for these ice cores is clearly of great scientific importance, but a reliable dating technique for the deepest parts of such cores, where the ice is older than about 10,000 years, does not exist [*Patterson*, 1984]. Since 1 kg of modern ice contains roughly the same amount of krypton as 1 L of modern groundwater, the sample processing and ^{81}Kr analysis for ice is analogous to the one outlined for groundwater.

Dating of very old groundwater is especially important in projects for a safe disposal of chemical and radioactive waste in geological formations. Whereas certain groundwaters are known to be very old, e.g., in the Great Artesian Basin in Australia [*Calf*, 1983] or in other aquifers in the USA, Canada, Africa, and Europe [*Davis and Bentley*, 1980; *Rudolph et al.*, 1983], absolute dating of such groundwaters is not easy. Recently, considerable progress has been made using the tandem accelerator mass spectrometer for the analysis of ^{36}Cl [*Bentley et al.*, 1982; *Phillips et al.*, 1983, 1984]. Our AQUI sample is an example of a groundwater that clearly illustrates the need for new dating techniques in the range of the ^{81}Kr method. Its age cannot be determined by any of the existing methods [*Schmassmann*, 1984]. The measured levels of ^{3}H (<0.7 TU) and ^{85}Kr (0.089 dpm/cc) show that the sample has no contribution of modern water; the ^{39}Ar activity (<5% modern) indicates an age of at least 1200 years; the ^{14}C value (<1.3% modern) is difficult to interpret because the very high δ^{13}C value (−3‰) shows that exchange processes between dissolved inorganic carbon and the rock matrix have occurred to a considerable degree, making ^{14}C model corrections uncertain. The low δ^{18}O value (−11.89‰) might be an indication that the water entered the aquifer during a cooler time, maybe as much as 20,000 or more years ago, during the last glaciation. But it can also be argued that the water is younger and originates from the nearby Limmat river with a measured δ^{18}O value of similar magnitude.

We hope that in the future investigations of very old aquifers, ^{81}Kr data will add valuable new information to give a better understanding of underground hydrology.

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